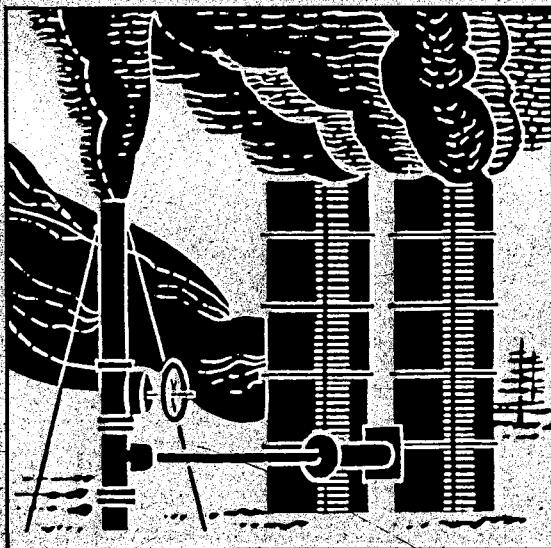


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THE OCCURRENCE OF PYRRHOTITE IN THE NGAWHA GEOTHERMAL SYSTEM, NEW ZEALAND

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SUMMARY

The Ngawha geothermal system is low in all sulphide minerals, but in comparison to systems in the Taupo Volcanic Zone it contains more widely distributed pyrrhotite which is currently depositing, mainly in fractures. This reflects the high proportion of vapour in the Ngawha system. Pyrrhotite is most common in the upper part of the reservoir and lower part of the aquitard. The Ngawha pyrrhotite is of monoclinic and monoclinic + hexagonal structure.

1. INTRODUCTION

The geothermal system at Ngawha is within the Quaternary-Holocene "Kerikeri volcanic field", and is sited on the central axis of the Northland peninsula (Fig.1). This system is the only known, active high temperature geothermal system outside the Taupo Volcanic Zone. The energy potential of the system was investigated by the Department of Scientific and Industrial Research (DSIR) and the Ministry of Works and Development (MWD) from 1977 to 1983. Fifteen holes were drilled, mostly 1000-1300 m, with the deepest Ng13 to a vertical depth of 2255 m.

Numerous studies were carried out on different components of the system, including the geology (e.g. Skinner, 1981; Cox and Browne, 1992), water and gas chemistry (e.g. Ellis and Mahon, 1966; Gigganbach and Sheppard, 1980; Sheppard 1984; Sheppard and Gigganbach, 1985; Cox and Browne, 1991) but also of the drill cores and cuttings and directed to petrology and hydrothermal alteration (Browne, 1980, 1981), isotope chemistry (Blattner, 1980, 1982), rock geochemistry and metallic mineralisation (Cox, 1984, 1985).

2. GEOLOGY OF NGAWHA SYSTEM

Within the geothermal area, thin basaltic lavas locally overlie 500-600 m of an extensive, chaotic sequence of marine sediments of Cretaceous-Tertiary age which contains many lithologies. These overlie and are interbedded with, an Eocene sequence of mudstones and sandstones (Skinner, 1981). The Eocene sequence lies on the basement rocks of the Permian-Jurassic Waipapa Group greywacke and argillites within which the deeper, hotter part of the reservoir occurs (Browne, 1980).

The Waipapa Group rocks have undergone regional metamorphism to greenschist facies, to temperatures of ~350°C (Mayer, 1968). Cores from Ngawha drillholes and surface exposures show that the greywackes and the argillites form beds from tens of centimetres to several metres thick. In appearance the rocks are typically dark grey-green, highly indurated, fine-grained, and cut by numerous narrow veins.

The overlying sedimentary rocks have low bulk permeabilities due to their fine-grained nature and high clay contents. These units therefore form a semi-confining layer

to the reservoir, which occurs within the greywackes and argillites. These have a low intrinsic permeability and near zero porosity, but the joints which serve as fluid channels typically have a spacing density of 15 per linear metre (Browne 1980). Permeability is therefore secondary and provided by associated fractures and joints. Channel permeability has been a major control on the intensity of the alteration and the identities of the secondary minerals formed. Permeability is highest in fracture zones and along the unconformity at the top of the greywacke/argillites.

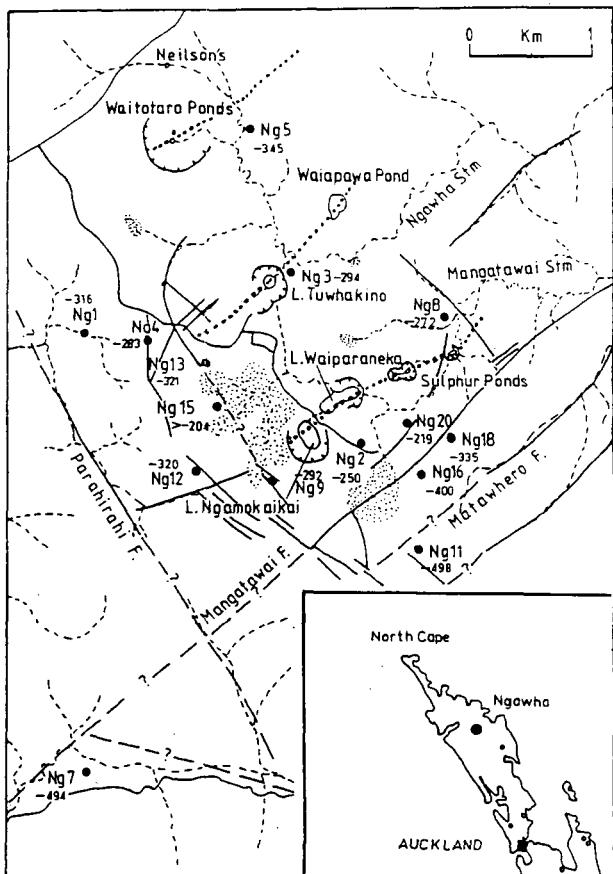


Fig. 1. Inset: location of Ngawha in North Island of New Zealand. Map: Ngawha drillfield showing faults, surface thermal features (hydrothermal eruption craters; three NE striking zones of surface activity; swamps) geothermal drillholes are shown with depth to basement (m RSL).

3. ROCKS AND METALLIC MINERALS

3.1 Samples and Analysis

A range of drill cores augmented by cuttings, was chosen to provide a representative selection of the secondary minerals present in the system. The samples were examined under binocular microscope, and thin sectioned. Specimens with pyrrhotite were further examined by SEM using semi-

quantitative EDAX analysis. The structures of the pyrrhotites were determined by XRD. For this the mineral, or material containing it, was hand picked, hand ground, and then pressed dry onto a glass slide. For XRD the following conditions were used: a goniometer rotation speed of 1/4 ° 2θ; chart drive of 2 cm/min; time constant of 4 sec; range of 10^2 , with monochromatic Cu-Kα radiation. Sample descriptions, in situ temperatures and XRD data are given in Table 1.

Table 1.

XRD ANALYSES OF PYRRHOTITES

SAMPLE	2θ d_{102}	2θ d_{202}	$d\bar{A}$ d_{102}	Type from XRD peaks*	N_{FeS}	Fe _t (atomic)	Meas. well T (°C)
Ng2,524.3m	43.95	44.15	2.0601	H << M	.938	46.9	220
	argillite; red-brown plates on joint surface; some clay (illite), quartz						
Ng3,982	44.05	44.25	2.0557	H << M	.931	46.6	225
	argillite; small, dull brassy plates in joint; some quartz and calcite						
Ng5,259.4	44.07	44.23	2.0548	M	.931	46.5	142
	brecciated siltstone; very small red-brown plates (< 0.5 mm) in fractures; also, calcite, quartz and pyrite						
Ng5,561	43.92	44.24	2.0614	M	.938	46.9	212
	jointed, silicified siltstone; minor, small grains and plates, mostly red-brown; some quartz, minor pyrite						
Ng5,920.7	43.98	44.18	2.0588	M ?	.932	46.6	236
	argillite; dark brassy, granular, in thin quartz veins; minor pyrite						
Ng12,648.5	44.05	44.27	2.0557	M	.931	46.6	228
	sheared argillite; common as brassy plates in quartz veins, some calcite veins; pyrrhotite only, fills some joints (< 0.25 mm)						
Ng13,730	44.00	44.13	2.0579	H < M	.932	46.6	220
	sheared argillite; red-brown plates with calcite, pyrite, trace quartz						
Ng13,815	43.98	44.22	2.0588	H < M	.932	46.6	222
	sheared argillite; red-brown plates with calcite, trace pyrite and quartz						
Ng9 (well)	43.7	-	2.0713	H	.958	47.9	c. 180-220
	well casing deposit (400-750 m); plates of black-brown pyrrhotite and quartz						
N51 (well)	43.94	44.04	2.0605	H << M	.938	46.9	c. 300
	well casing deposit, HGP-A, Hawaii; 1189-1219 m; black plates, some anhydrite; sample is oxidised						
PN9, RD	43.96	-	2.0597	H	.937	46.9	c. 320
	Southern Negros, Philippines, 3130 m, andesite; dark brassy grains to 0.5 mm, replacement of rock matrix						

3.2 Other Sulphide Minerals

Base metal sulphide minerals are of low abundance in the surface and subsurface samples and only local concentrations occur (e.g. as narrow veins). The decreasing order of abundance of sulphides within the reservoir rocks is: pyrite (major), pyrrhotite (common), arsenopyrite (minor), chalcopyrite (trace) and sphalerite (trace). Currently, minor pyrite, sulphur, cinnabar, and occasionally elemental mercury, plus traces of realgar, orpiment and stibnite are depositing at the surface.

Although pyrite is the most common sulphide, it is much less abundant at Ngawha than it is in other New Zealand geothermal systems (e.g. Browne, 1978) and at Ngawha it rarely forms more than 5% of a sample. Pyrite occurs in both the reservoir and overlying aquitard, and in impermeable zones in metasediments where it is imbedded within the fine-grained rock matrix. Both pyrite and pyrrhotite are most common in the upper parts of the reservoir. The greatest abundance of pyrite is in core from Ng5, 547 m, a coarse-grained glauconitic sandstone at the base of the aquitard. This is the most mineralised core from Ngawha, and contains

14.4% of Fe and of 5.5% S.

A mineralised zone occurs at a depth of around 720-850 m in drillhole Ng13. This zone is highly fractured and may be a fault intersection; coring was not possible, and drilling fluid losses were high here (MWD unpub. report). Cuttings from 700-940 m depth contain widespread sulphides and calcite. SEM examination of cuttings from Ng13, 730 m depth revealed well-crystallised arsenopyrite, with pyrrhotite and pyrite present in veins of calcite and quartz.

3.3 Distribution of Pyrrhotite

Although pyrrhotite is not abundant at Ngawha it is widespread (Fig. 2) and more common here than in other New Zealand systems. Pyrrhotite was reported in cores from drillhole Ng1, and from the upper part of the reservoir at ~540-580 m (Steiner and Rafter, 1966). Cuttings from Ng15, a hole drilled to only 431 m, contain well developed pyrrhotite and calcite in a strongly jointed and brecciated siltstone at around 317 m depth. This zone may be a fault along which fluids, mainly vapour, ascend.

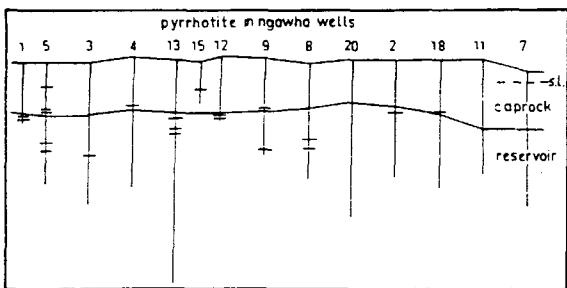


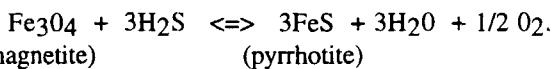
Figure 2- Generalised N-S profile through the drillfield showing geothermal wells and locations where pyrrhotite was identified in cores and cuttings.

Greywackes and argillite with minor pyrrhotite occur in cores and cuttings from drillhole Ng8 in the east, a zone with cooler groundwater inflow. However, pyrrhotite was not found in drillhole Ng11, nor Ng7, both located outside the system and in an outflow region. Within the reservoir, the absence of pyrrhotite in samples from drillholes Ng16 and Ng20 and its rare occurrence in Ng18, is interpreted as due to the lower permeability of the rocks intersected by these drillholes.

Pyrrhotite is typically present within (current) permeable zones, and in many cases it is also associated with calcite, or less commonly, quartz. Such zones are characterised by shearing, brecciation and jointing. Textural evidence shows that where pyrite is present it is usually older than the pyrrhotite, and virtually all the pyrrhotite appears to be of current or very recent origin. Most of the pyrrhotite occurs

as distinct plates, up to 0.5 mm thick, deposited on joint surfaces (Fig. 3a) but it also occurs with other vein minerals, and less commonly it is present within the matrix of the rock. The pyrrhotite crystals at Ngawha are smaller than those at Ohaaki, which are up to 4 mm in diameter (Weissberg et al., 1979).

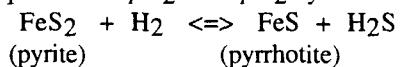
Material consisting largely of pyrrhotite and calcite has deposited on the casing of Ng9 at depths between 400 and 750 m, most likely in response to boiling during production testing (Fig. 3b). This pyrrhotite is probably derived from magnetite formed from the well casing itself, as this would be unstable above $\sim 150^{\circ}\text{C}$ (e.g. Steiner, 1977) and be replaced, at least partly, by pyrrhotite:



4. CHARACTER OF PYRRHOTITE

4.1 Type of Pyrrhotite

Pyrrhotite and pyrite are the two most common Fe sulphides that result from the alteration of rocks (Browne and Ellis, 1970), and their relative stabilities can be related to the measurable parameters $p\text{H}_2\text{S}$ and $p\text{H}_2$ by the reaction:



Although pyrite is of near stoichiometric composition (e.g. Dana, 1959), pyrrhotite is of variable composition. This non-stoichiometric character of pyrrhotite is due to a structural defect that produces an Fe deficiency and so it has a formula expressed as Fe_{1-x}S (where x varies from 0 to ~ 0.125) (e.g. Deer et al., 1962). The concentrations of H_2S and H_2 in the fluid are buffered by coexisting pyrite and chlorite (e.g. Barton and Skinner, 1979) and the assemblage pyrite + pyrrhotite + magnetite may buffer oxygen and sulphur fugacities (e.g. Crerar et al., 1978). Deposition of the iron sulphides from thermal fluids may occur (in the presence of an adequate supply of Fe) by changing oxygen and sulphur concentrations, such as by cooling, an increase in pH, or dilution of the thermal fluid. A mineral with variable composition such as pyrrhotite may therefore reflect the local fluid conditions prevailing at the time of its formation.

4.2 Composition of Pyrrhotite

Semi-quantitative (SEM-EDAX) analyses for Fe and S in pyrrhotites were not successful, and produced Fe values inconsistent with those determined by XRD ($\pm 3\%$ Fe). This was especially the case where the samples had oxidised, or where other hosts of Fe (e.g. magnetite or pyrite) were present. An approximate estimate of the Fe contents of the pyrrhotites was made from the position of the d_{102} reflection (unheated; see Arnold, 1969), then by finding the N_{FeS} value (from Toulmin and Barton, 1964) and converting this to atomic % Fe.

X-ray diffractograms (Fig. 4) show a typical single peak (102) for hexagonal pyrrhotite, whereas monoclinic pyrrhotite has a double peak with typical separations of $0.350^{\circ}\text{2}\theta$ (Arnold, 1966). Mixtures of hexagonal and monoclinic pyrrhotite, and with at least 20% of each, typically show a reduced intensity of the (202) reflection (Arnold, 1966).

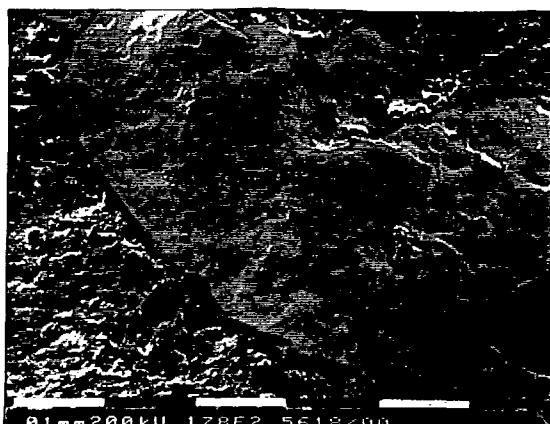


Figure 3- Electron micrographs of pyrrhotite showing scale bars, (a) Ng12, 648 m: pyrrhotite plate on barren joint in brecciated argillite; (b) Ng9 casing, 400-750 m: dominantly pyrrhotite plates, but also contains calcite and quartz.

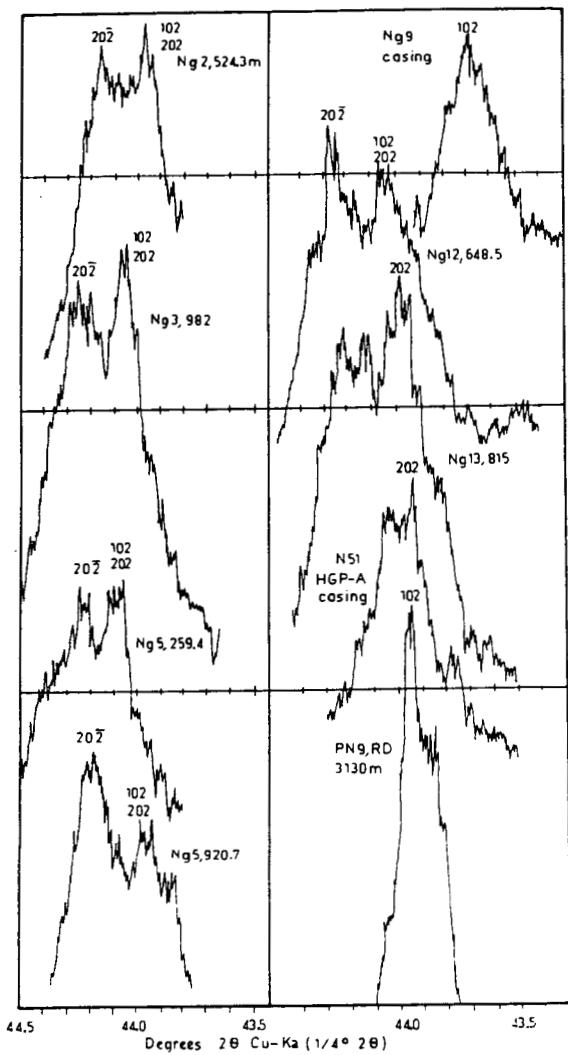


Figure 4- X-ray diffractograms of geothermal pyrrhotites described in Table 1.

4.3 Pyrrhotite-Pyrite Stability Fields

The relative stability of these two sulphides at different temperatures can be shown by considering pH_2S/pH_2 ratios (Fig. 5). As H_2 is very insoluble it fractionates more readily into vapour than H_2S (e.g. Ellis and Mahon, 1977) therefore, where boiling occurs the residual fluid loses H_2 preferentially, and acquires a higher H_2S/H_2 ratio which favours pyrite formation. The separated vapour, however, has a lower ratio, having gained relatively in H_2 . Rocks exposed to steam which has boiled from deeper water may, therefore, deposit pyrrhotite (Browne and Ellis, 1970).

Compared to the deep fluids of most other New Zealand geothermal systems (e.g. Weissberg et al., 1979), almost all Ngawha wells (before vapour loss) plot either close to the pyrite-pyrrhotite equilibrium line, or within the pyrrhotite stability field. Fluids with these low H_2S/H_2 ratios reflect the typically high proportion of vapour in the fluids at Ngawha. Most vapour-dominated systems (e.g. The Geysers & Larderello) have fluids with proportionally higher H_2 (e.g. Ellis and Mahon, 1977; Henley et al., 1984). As these systems occur in sedimentary rocks it is possible that their H_2 may derive from organic material.

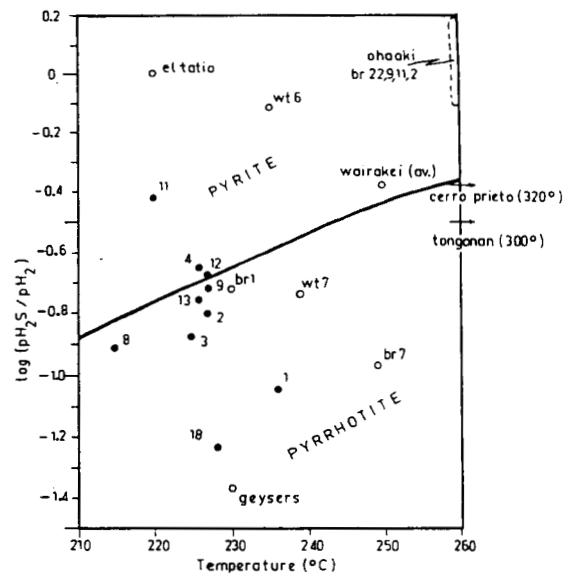


Figure 5- Pyrrhotite-pyrite equilibrium phase diagram in respect to pH_2S/pH_2 (after Browne and Ellis, 1970). Ngawha wells are closed circles. Open circles is data from other areas (Ellis and Mahon, 1977; Hedenquist, 1983; Henley et al., 1984; Hedenquist and Henley, 1985).

4.4 Pyrrhotite in Other TVZ Systems

Steiner (1977) identified six pyrrhotite samples from Wairakei as monoclinic. This, however, does not appear to agree with their Fe contents as deduced from the "d" location which indicate a hexagonal structure. Steiner (1977) also identified two samples from Waiotapu as monoclinic (Wt 5, 320-322 m) and one as mixed monoclinic-hexagonal (Wt 6, 899-901 m). Hedenquist (1983) X-rayed five pyrrhotites from Waiotapu and identified them as hexagonal; their Fe contents, estimated from reported d_{102} values, however, indicate one to be monoclinic. Kissin and Scott (1982) determined the Fe content of four pyrrhotites from Ohaaki (BR 4, 12, 13) and judged them to be monoclinic (Fig. 6).

5. DISCUSSION AND CONCLUSIONS

The results show that the Ngawha pyrrhotites are all either monoclinic or a mixture of monoclinic+hexagonal types (Fig. 6). Those from Ohaaki are similar to the Ngawha samples and are also monoclinic; Wairakei samples also appear to be monoclinic. Pyrrhotites from Ohaaki and Wairakei are similar in form and occurrence to those at Ngawha but form larger crystals (often filling barren joints). This and their association with veins supports the conclusion that pyrrhotite is currently depositing here.

The pyrrhotite deposited in the Ng9 casing is hexagonal (Fig. 4) but its presence required external Fe and boiling with gas separation. The Southern Negros sample from drillhole PN9, at a depth of 3130 m, is also hexagonal and its composition plots near the pyrrhotite-pyrite equilibrium line (Fig.6). This sample pre-dates the present geothermal regime and appears to be compatible with the stability field in which it plots. The casing deposit from drillhole HGP-A (Hawaii) probably formed at $\sim 300^\circ\text{C}$ which is above the 254°C stability line for monoclinic pyrrhotite (Kissin and Scott, 1982). However, its XRD pattern (Fig. 4) suggests it is a mixture of monoclinic and hexagonal pyrrhotite; this

inconsistency is probably a result of its "artificial" formation.

The main conclusion is that most of the pyrrhotite at Ngawha has deposited during the current thermal regime and is monoclinic or monoclinic+hexagonal in structure. Although the distribution of pyrrhotite is largely controlled by permeability, fluid composition is important and the presence of the mineral reflects the conditions of its

deposition. Fluids with low H_2S/H_2 ratios (e.g. drillholes Ng1 and Ng18) have the greatest tendency to deposit pyrrhotite; this tendency decreases with boiling as the fluid composition passes into the pyrite stability field (drillhole Ng4); with further boiling the residual liquid gains a higher H_2S/H_2 ratio making pyrite the stable iron sulphide phase (e.g. Ng11; outflow zone of "degassed" cooling water).

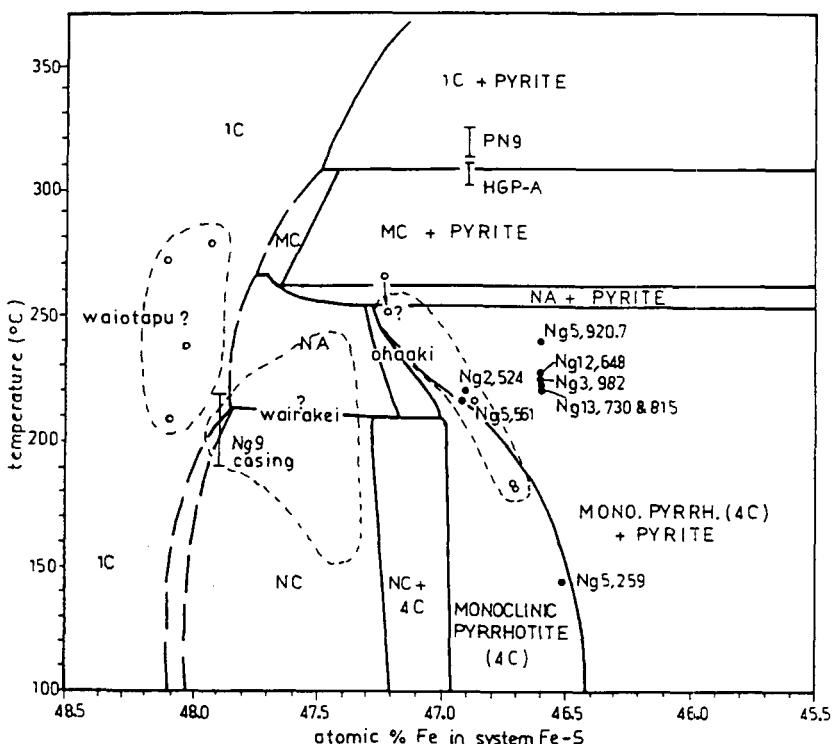


Figure 6- Phase diagram for pyrrhotite types, in respect to temperature and Fe content (atom.%), also showing pyrrhotite superstructure types (after Kissin and Scott, 1982). Ngawha samples are solid circles. Exact in situ temperatures are not known for the casing deposits. Data for other areas: Ohaaki (Kissin and Scott, 1982); Waiotapu (Hedenquist, 1983); Wairakei (Steiner, 1977).

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